

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF POLYETHER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polyether in productivity improved as a result of a shortened induction period by polymerizing a monoepoxide through ring opening in the presence of an initiator, an assistant for developing initial activity and a compound metal cyanide compound complex catalyst.

SOLUTION: A polyether (e.g. polyoxyalkylene polyol) is produced by polymerizing a monoepoxide through ring opening at 50-150°C in the presence of an initiator being a polyhydroxy compound having 2-8 hydroxyl groups, 1-5,000ppm, based on the initiator, of an assistant for developing initial activity being an active-hydrogen-free nitrogenous low-molecular compound and 1-5,000ppm, based on the initiator, of a compound metal cyanide complex catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the polyether which used the composite metal cyanide compound complex compound catalyst.

[0002]

[Description of the Prior Art]Conventionally, it is considered as the catalyst to which the ring opening reaction of the monoepoxide, such as alkylene oxide, is carried out, and the composite metal cyanide complex is known (3278457 to US9 specification). The manufacturing method of the composite metal cyanide complex catalyst used at this time is proposed by US3427256, US3941849, US4472560, US4477589 specification, etc.

[0003]

[Problem(s) to be Solved by the Invention]The composite metal cyanide complex catalyst is known as a catalyst which are high activity, a long life, and low side reaction nature, and can manufacture the polyether of narrow molecular weight distribution. When manufacturing polyether using a composite metal cyanide complex catalyst, an induction period is usually needed.

[0004]That is, even if a composite metal cyanide complex catalyst mixes an initiator with monoepoxide, a monoepoxide ring-opening-polymerization reaction does not occur immediately, but it is necessary to activate a composite metal cyanide complex catalyst by a small amount of monoepoxide, and the time of until [this] it is activated is called induction period. Usually, to shorten an induction period more from a viewpoint of a productivity drive for 30 minutes - several hours for this reason was desired.

[0005]It was not an effective method, although the mechanism to which ring opening polymerization of the monoepoxide of a composite metal cyanide complex catalyst is carried out was not necessarily clear, and the induction period became short somewhat when the

physical shape of a catalyst, the presentation of a catalyst, a crystallized state, or impurity quantity was changed.

[0006]Although it was known that an induction period will become short by making the concentration of the monoepoxide mixed with an initiator increase, after the catalyst was activated, since a reaction occurred in Itsuki, calorific value increased, and there was a problem which has an adverse effect on the polyether obtained.

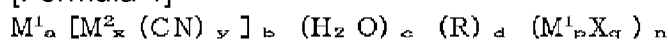
[0007]

[Means for Solving the Problem]This invention is the following invention made that the above-mentioned problem should be solved. A manufacturing method of the polyether carrying out the ring-opening-polymerization reaction of the monoepoxide under existence of an initiator and an initial activity manifestation auxiliary agent using a composite metal cyanide complex catalyst.

[0008]It is thought that a composite metal cyanide complex catalyst in this invention has the structure of ** 1, for example. In ** 1, an anion in which M^1 and M^2 form metal, R forms an organic ligand, and X forms M^1 and a salt, a, b, c, d, n, x, y, p, and q are integers which change with a metaled valence and the coordination number.

[0009]

[Formula 1]



[0010]As M^1 , Zn(II), Fe(II), and Fe(III), It is preferred to use one or more sorts chosen from Co(II), nickel(II), Mo(IV), Mo(VI), aluminum(III), V(V), Sr(II), W(IV), W(VI), Mn(II), Cr(III), Cu(II), Sn(II), and Pb(II). It is preferred to use Zn(II) or Fe(II) especially.

[0011]It is preferred to use as M^2 one or more sorts chosen from Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III) nickel(II), V(IV), and V(V). It is preferred to use Co(III) or Fe(III) especially.

[0012]R is an organic ligand and can be preferably chosen from ether, ester, alcohol, aldehyde, ketone, amide, nitril, and a sulfide.

[0013]Specifically, for example Mono- glyme (ethyleneglycol dimethyl ether), A jig lime (diethylene glycol dimethyl ether), Tori Gleim (triethylene glycol wood ether), i-propanol, t-butanol, n-butanol, i-butanol, t-pentanol, i-pentanol, N,N-dimethylacetamide, or dioxane is mentioned. Mono- glyme, a jig lime, t-butanol, etc. are preferred.

[0014]A composite metal cyanide complex catalyst, For example, cyano methacrylate $Z_f [M^2_x (CN)_y]_g$ which makes a component solution and M^2 of metal salt $M^1_p X_q$ which makes M^1 a component (Z is hydrogen, an alkaline metal, etc.) f and g are integers. It is obtained by mixing, making solution react, contacting the organic ligand R and making it configurate

further.

[0015]Polyether is manufactured by making a catalyst exist in a mixture of monoepoxide and an initiator, and making it usually react to it, and an initial activity manifestation auxiliary agent is made to live together in this invention in the case of this reaction. It can also react adding monoepoxide to the system of reaction gradually, and an initial activity manifestation auxiliary agent may be added with monoepoxide.

[0016]Although a reaction occurs also under ordinary temperature, it may heat or cool the system of reaction as occasion demands. Usually, 100-130 °C of 50-150 °C is adopted preferably. If it exceeds 150 °C, since physical-properties aggravation of polyether will be caused, it is not desirable.

[0017]Although the amount in particular of catalyst used is not limited, about 1-5000 ppm is suitable to an initiator to be used, and 30-1000 ppm is more preferred. Introduction to the system of reaction of a catalyst may be first put in block, may be introduced, may be divided one by one and may be introduced.

[0018]It is preferred that it is a nitrogen-containing low molecular weight compound which does not have active hydrogen as an initial activity manifestation auxiliary agent used in this invention. Although a mechanism of this invention is not in detail, existence of a nitrogen atom is considered to have influenced activation of a composite metal cyanide complex catalyst.

[0019]Since the 1st class amino group, the 2nd class amino group, a hydroxyl group, etc. have active hydrogen, it is thought that a compound which has such a functional group is not suitable as an initial activity manifestation auxiliary agent.

[0020]As for the number of nitrogen atoms contained in one molecule of an initial activity manifestation auxiliary agent, 1-5 pieces are preferred, its 1-3 pieces are more preferred, and especially its one piece is preferred. As for the number of carbon atoms, 20 or less pieces are preferred, and especially its ten or less pieces are preferred.

[0021]As a nitrogen-containing low molecular weight compound which does not have active hydrogen, trialkylamine, tetra alkyl diamine, tertiary amine content cyclic amine, N,N-dialkyl amide, etc. are mentioned.

[0022]As trialkylamine, there are trimethylamine, triethylamine, tributylamine, triamylamine, N,N-dimethylcyclohexylamine, diethylbenzylamine, etc.

[0023]There are N,N,N',N'-tetramethylethylenediamine etc. as tetra alkyl diamine.

[0024]As tertiary amine content cyclic amine, N-methylmorpholine, a N,N'-dimethylpiperazine, There are 1,5-diazabicyclo [4.3.0] non-5-ene, 1,8-diazabicyclo [5.4.0] undec-7-ene, 1,4-diazabicyclo [2.2.2] octane, etc.

[0025]As N,N-dialkyl amide, N,N-dimethylformamide, N,N-dimethylacetamide, an N-methyl-N-ethylacetamide, There are an N-methyl-N-propylacetamide, a N,N-diethylacetamide, N,N-dimethylpropionamide, N,N-dimethyl butaneamide, N,N-dimethylaceto acetamido, N,N-

dimethylaceto propionamide, etc.

[0026]As an initial activity manifestation auxiliary agent, N,N-dialkyl amide is preferred, and especially N,N-dimethylacetamide is preferred.

[0027]As for especially the amount of initial activity manifestation auxiliary agent used, it is preferred to use 5-2000 ppm 1-5000 ppm to an initiator.

[0028]As polyether obtained by a method of this invention, polyoxyalkylene polyol is preferred. Polyoxyalkylene polyol carries out the ring-opening addition reaction of the monoepoxide to an initiator which has at least two hydroxyl groups one by one.

[0029]A polyhydroxy compound which has 2-8 hydroxyl groups especially as an initiator is preferred. As a polyhydroxy compound, for example Dihydric alcohol, such as ethylene glycol and propylene glycol, Trihydric alcohol, such as glycerin, trimethylolpropane, and hexanetriol, There is polyether of low molecular weight rather than an object produced by making monoepoxide react to alcohol more than tetravalence, such as pentaerythritol, diglycerol, glucose, sorbitol, and a shook sirloin, and these alcohol.

[0030]The polyether of low molecular weight can be used rather than an object produced by making monoepoxide react to amines, such as phenols, such as bisphenol A, ethanolamine, diethanolamine, and ethylenediamine. These polyhydroxy compounds may use two or more sorts together.

[0031]This invention is applicable also to a method of carrying out the ring opening reaction of the monoepoxide to a univalent initiator, and manufacturing a polyether monooar again. As a univalent initiator, there is polyether of low molecular weight, for example rather than unsaturation group content mono- hydroxy compounds, such as monooars, such as methanol and ethanol, and allyl alcohol, and an object produced by making monoepoxide react to these.

[0032]Although a molecular weight in particular of an initiator is not limited, about 70 or more are preferred. In early stages of a reaction, as for a thing of low molecular weight, monoepoxide cannot react as easily as this. Although a maximum of a molecular weight of an initiator changes also with the molecular weights of the polyether made into the purpose, about 2000 or less and about 1500 or less are preferred.

[0033]Monoepoxide in this invention has with a carbon numbers of two or more preferred monoepoxide, and its monoepoxide of the carbon numbers 2-4 is preferred. Propylene oxide (PO), 1,2-butylene oxide, 2,3-butylene oxide, epichlorohydrin, ethylene oxide, etc. are specifically preferred, and PO is the most preferred.

[0034]As for a hydroxyl value of the polyether obtained, 5-40 are preferred.

[0035]Polyether polyol obtained by this invention is the most useful as polyol for polyurethane stock which is independent [its], or uses together with other polyols and is used. A polyether poly(or mono-) oar obtained by this invention is used also for a raw material of synthetic resins other than polyurethane, or a use of an additive agent. It can be used as a lubricating oil,

electrical oil, hydraulic oil, other oils, or a raw material of those. The polyether obtained by this invention is changed into other compounds, such as an alkyl ether ghost and an acylation thing, and it can be used for various uses.

[0036]

[Example]Although an example (Examples 1-3) and a comparative example (Examples 4-6) explain this invention concretely below, this invention is not limited to these.

[0037][Examples 1-5] In autoclave, as an initiator Polyoxypropylene triol (molecular weight 1000), The zinhexacyano cobaltate MONOGURAIMU system catalyst of the quantity shown in N,N-dimethylacetamide (DMA) and the table of the quantity shown in a table to this triol was taught, and after carrying out temperature up to 120 **, PO was added 10% of the weight to the initiator.

[0038]Time until the fall and generation of heat of a pressure by PO being consumed are accepted was measured as an induction period. The highest arrival temperature was measured for measurement of the temperature change accompanying generation of heat. A result is shown in a table. Then, 400% of the weight of PO was added over 4 hours to the initiator, and the polyether polyol of the molecular weight 5000 was obtained.

[0039][Example 6] The addition of PO after carrying out temperature up to 120 ** was made into 20 % of the weight instead of 10 % of the weight, and also an induction period and the highest arrival temperature were measured like Example 4. A result is shown in a table. Then, 400% of the weight of PO was added over 4 hours to the initiator, and the polyether polyol of the molecular weight 5000 was obtained.

[0040]Compared with Examples 4 and 5, the induction period of Examples 1-3 was dramatically short, and especially the examples 2 and 3 were like [to which generation of heat is accepted simultaneously with introduction of PO]. Example 6 raised the concentration of PO -- a sake -- an induction period -- comparatively -- alike -- short -- becoming -- **** -- although - the highest arrival temperature -- it is high -- that is, it seems that calorific value became high since the reaction of PO occurred in Itsuki. Therefore, when it comes to physical-properties aggravation of polyether, and the cause of inactivation of a catalyst, it thinks, and is disadvantageous.

[0041]

[Table 1]

	DMA添加量	触媒添加量	誘導時間	最高到達温度
例1	1 0 p p m	3 0 0 p p m	5 分	1 3 0℃
例2	3 0 0 p p m	3 0 0 p p m	0 分	1 2 9℃
例3	1 0 0 0 p p m	3 0 0 p p m	0 分	1 3 0℃
例4	0 p p m	3 0 0 p p m	4 0 分	1 2 7℃
例5	0 p p m	2 0 0 0 p p m	4 0 分	1 2 7℃
例6	0 p p m	3 0 0 p p m	3 0 分	1 5 2℃

[0042]

[Effect of the Invention]The induction period at the time of polymerizing PO using a composite metal cyanide complex catalyst can be shortened substantially, the productivity of polyether is raised, and it gets.

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CLAIMS

[Claim(s)]

[Claim 1]A manufacturing method of the polyether carrying out the ring-opening-polymerization reaction of the monoepoxide under existence of an initiator and an initial activity manifestation auxiliary agent using a composite metal cyanide complex catalyst.

[Claim 2]A manufacturing method of claim 1 which is a nitrogen-containing low molecular weight compound in which an initial activity manifestation auxiliary agent does not have active hydrogen.

[Claim 3]A manufacturing method of claim 2 whose initial activity manifestation auxiliary agents are N,N-dialkyl amide.

[Claim 4]A manufacturing method of claim 3 whose initial activity manifestation auxiliary agent is N,N-dimethylacetamide.

[Claim 5]A manufacturing method of claim 1, 2, 3, or 4 which uses 1-5000 ppm of initial activity manifestation auxiliary agents to an initiator.

[Translation done.]